2.0 LITERATURE REVIEW

2.1 General

This section provides an overview of previous studies conducted by researchers in the field of intumescent fire protective coatings for steel. The characteristics and properties of various flame retardant additives, fillers and binders were reviewed prior to the synthesis of the intumescent coating in this study. The chemical and physical mechanism of intumescence when exposed to fire or heat was studied. A brief review of steel's properties at elevated temperature and standard time-temperature fire curves was also done.

2.2 Thermal Degradation, Flame Retardancy and Flammability

Organic and inorganic compounds degrade thermally when exposed to heat. If this thermal degradation of the combustible materials is oxidative and characterized by the generation and emitting of heat and light, the process is called a fire. The light emitted from the fire is the flame, which is a visual sign and is an indication of the heat generated.

Combustion is usually a gas phase phenomenon. Volatile combustible species oxidize exothermically in the gas phase. Afterglow or glowing combustion is a form of non-gas phase combustion. Here the substrate is oxidised in the condensed phase to form both solid and gaseous products. This usually takes place at temperatures well below the ignition temperature of the material. For instance, the carbon residue in a carbon rich material is oxidised in the solid phase.

Emman's fire triangle is generally used to illustrate how combustion works and is shown in Figure 2.1 (Wolf and Lal Kaul, 1992). For a sustained fire, three elements are needed as follows (Sutker, 1988):

- Fuel- Volatile combustibles from carbon rich substance
- Heat- Supplied by the exothermic oxidative destruction of fuel
- Oxidising agent- Oxygen provided by air

On thermal decomposition, the polymer releases smaller volatile compounds that act as fuel to the fire. These combustible species mix with the oxygen in the air to form an ignitable mixture. Exothermic oxidation of the volatiles occurs and the material burns. Light and more heat are generated. The process becomes self-sustaining and functions with a feedback loop as can be seen in the fire triangle (Figure 2.1). The product of the fire differs for each combustible compound. In the case of polymers, the gases produced by combustion tend to be mainly carbon dioxide (CO_2), carbon monoxide (CO) and water vapour (H_2O). The solid residue is mostly carbon (C) and ash (oxidised metals) (Sutker, 1988; Wolf and Lal Kaul, 1992).

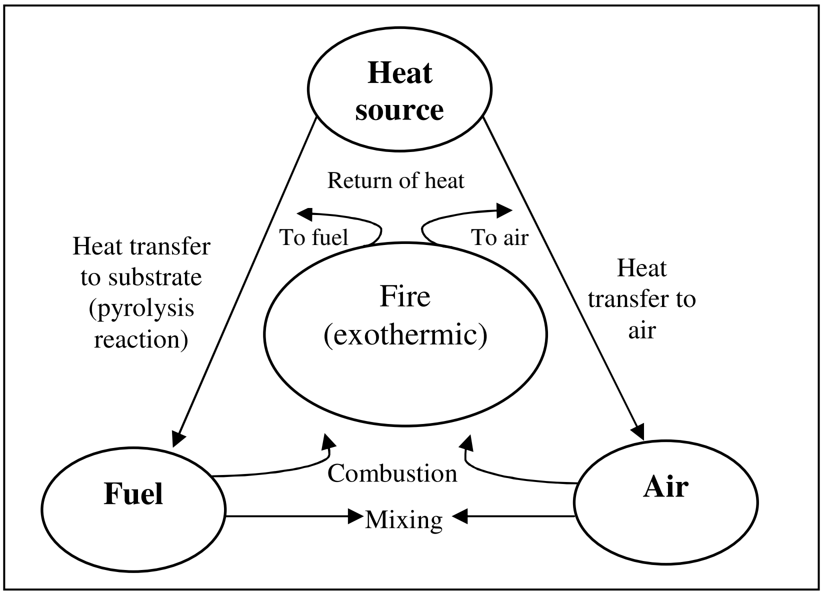


Figure 2.1 Emman's fire triangle (Wolf and Lal, 1992)

A flame retardant system is a compound or compositions added to materials, which increases a given material's resistance to combustion. An effective flame retardant need to hinder the supply of one or more of the elements required for sustained combustion (Sutker, 1998). The objective of flame retardant is to lower the combustion materials' inherent fire risk by lowering the rates of combustion and flame spreading under fire conditions (Benbow, 1987). The use of flame retardants may prevent a small fire from becoming a major catastrophe (Green, 1996). In order for a flame retardant to be effective, it must interact and interfere with degradation of the host polymer at the polymer's degradation temperature (Schmidt, 1965). The degradation temperatures for the most widely used polymers are between 200°C and 400°C (Pearce, 1986). Increased fire resistance can be achieved through several mechanisms as shown in Figure 2.2 (Focke et al., 1997). The interference with the combustion process may take place in the gas or vapour (flame zone) or condensed or solid phases (polymers melt).

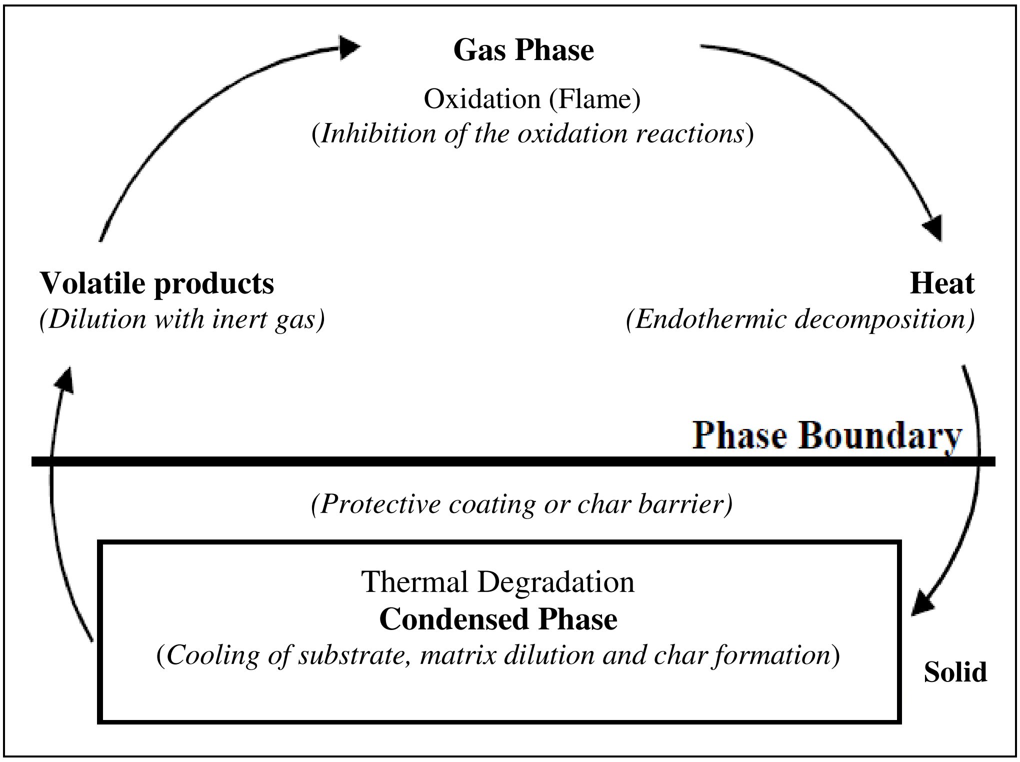


Figure 2.2 A simplified model for combustion and flame retardancy

A flame retardant is not designed to prevent the material from igniting, but to keep the flame spread rate to a minimum and prevent sustained burning. Flame retardants tend to retard the spread of flames by increasing the given polymer's resistance to ignition. Ignition is unavoidable, because most substances will flame up if subjected to high enough levels of fire stress-thermal radiation (Sutker, 1988).

A complete and useful description of the mechanisms of general retardant systems is provided in the review articles of Green (1996 and 1997). Different flame retardant systems can be identified, all of which function by different mechanisms. Flame retardants interfere with the thermal decomposition pathway of the polymeric material. Different compositions interact differently with different polymers and a flame retardant's use is thus very specific to the particular substrate for which it was designed.

The use of halogen containing flame retardants started to grow in the 1970's. The 1980's saw a large increasing in the use of brominated systems. Some halogen flame retardants which form acids during combustion operate through gas-phase free-radical inhibition. Halogen based flame retardants function in the vapour phase. On heating, they decompose to form halogen radicals. These halogen radicals interfere with the oxidation of the volatile fuels. They react with the oxygen and hydrogen radicals in the gas phase, thereby reducing their concentration and extinguishing the fire (Lyons, 1987; Pettigrew, 1993; Georlette et al., 2000). Antimony and phosphorus based compounds are very effective synergists with halogen based flame retardants (Touval, 1993; Weil, 1993). These compounds help with the scavenging of free radicals and regeneration of the halogen radicals.

In the 1990’s the market started to move away from halogen based flame retardants (Green, 1997). This is because they produce toxic gases such as hydrobromic and hydrochloric acid fumes with high levels of smoke. These gases are also highly corrosive. The halogen containing retardants are also difficult to dispose, which implies that they are an environmental risk (Green, 1997; Pettigrew, 1993). The shift to more environmentally friendly flame retardants is of interest worldwide but especially in Europe. The majority of current research focuses on non-halogen systems. However, alternative systems are usually less effective and more expensive (Mount, 1992).

Other groups of retardants produce many non-combustible gases and dilute the amount of fuel or oxygen supplied to the fire. The formation of solid residues on the surface of the burning material is another way of reducing flame spread. Some reduce the rate of heat release during combustion by affecting the heat transfer pathway to the polymer substrate. Another group of flame retardants form a foaming char on the surface of the combusting material. These additives are called intumescent systems. A system can also operate through combinations of the above-mentioned mechanism (Green, 1996).

The following terms and definitions are used to describe the different mechanisms by which flame retardants operate (Pettigrew, 1993):

- **Inert gas dilution:** Large quantities of inert and non-combustible gases are produced on thermal decomposition of the additive. The concentration of oxygen and combustible species are reduced and the fire stops.
- **Thermal quenching:** The surface temperature of the polymer is reduced or kept low by the endothermic degradation of the additive. Due to the lower substrate temperature, less combustible products are produced and the thermal degradation is retarded.

- **Physical dilution:** Large quantities of inorganic fillers are added to the polymer matrix. The amount of flammable material is thus reduced and the substrate's fire resistance increased.
- **Chemical interaction:** Some flame retardants thermally dissociates into radical species that then interferes with the gas phase combustion of the combustibles.
- **Protective char:** On thermal decomposition, the additive forms an insulating char barrier on the surface of the polymer. This char reduces heat transfer to the polymer, diffusion of oxygen to the area of decomposition and diffusion of combustibles to the flame zone, retarding the combustion.

An ideal flame retardant will have the following properties (Gann, 1993; Green, 1996; Green 1997; Sutker, 1988; Wolf and Lal Kaul, 1992; Miller, 1995):

- It reduces flammability to the required standard;
- It is thermally stable at the processing temperatures;
- Have a long term compatibility with the polymer matrix;
- Maintains or improves the mechanical properties of the polymer;
- Represents no health hazard; and
- Cost effective.

2.3 Fire Protective Surface Coatings

A common method to protect substrates from fire is to use an insulating coating. The ideal coating should possess the following properties: non-flammability, low thermal conductivity, strong adhesion to the surface substrate, environmentally durable, wear resistant, light-weight, thin and inexpensive. There are hundreds of coating materials that are commercially available for use on structural elements, although none possess all the properties required for an ideal coating.

There are three major classes of insulating coatings: flame retardant polymers, thermal barriers, and intumescent coatings. Flame retardant polymers are inherently fire resistant organic resins (e.g. brominated polymers) or inorganic materials (e.g. geopolymers) that are applied as a thin film (usually less than 5 mm) over the composite substrate. These polymers delay ignition and flaming combustion of the substrate due to their high thermal stability and, in the case of inorganic polymer coatings, low thermal conductivity. Thermal barrier coatings are usually ceramic-based materials that are non-flammable and have low heat conducting properties. Examples of these coatings include ceramic fibrous mats (e.g. silica, rock wool) and ceramic plasma-sprayed films (e.g. zirconia). Intumescent materials provide fire protection by undergoing a chemical reaction at an elevated temperature that causes the coating to foam and swell. This reaction process produces a highly porous, thick char coating that has a very low thermal conductivity to protect composite materials against fire (Borown et al., 1995; Sorathia and Beck, 1996; Sorathia et al., 2003).

2.4 Intumescent Coatings

Intumescent coatings provide fire protection by undergoing an endothermic decomposition reaction process at the elevated temperatures that causes the material to swell and foam into a highly porous, thick and thermally stable char layer (Vanderall, 1971; Kay et al., 1979; Camino et al., 1989; Kandola and Horrocks, 1997). The high void content and thickness of the coating allow it to act as an insulation barrier to the underlying substrate against flame and heat.

An intumescent coating can be applied by painting or spraying a liquid compound onto structural elements. The compounds cure in the air over several hours into a solid intumescent film. The maximum coating thickness that can be achieved with this method is under about 5 mm. Thicker coatings are applied by bonding of fibrous intumescent mat directly onto the substrate using high-temperature adhesive paste. The fire protection provided by intumescent coatings occurs by three reaction processes (Kay et al., 1979; Camino et al., 1989; Kandola and Horrocks, 1997):

- the coating material decomposes,
- inert gases evolved from the decomposition reaction are produced at a high enough rate to drive back hot convective air currents, and most importantly,
- the coating expands into a highly porous char layer with a high resistance to heat conduction from the flame into the underlying composite substrate.

Intumescent coatings consist of a mix of compounds that each has a role in the intumescence process. The four main types of compounds are a carbon-rich (carbonific) compound, inorganic acid or acid salt, organic amine or amide, and a blowing agent (spumific). For intumescence to occur these compounds must undergo a series of decomposition reactions and physical processes almost simultaneously, but within a proper sequence. The order of these processes is given in Figure 2.3. If the time between the processes is too long or they do not occur in the correct order, then the coating will fail to intumesce.

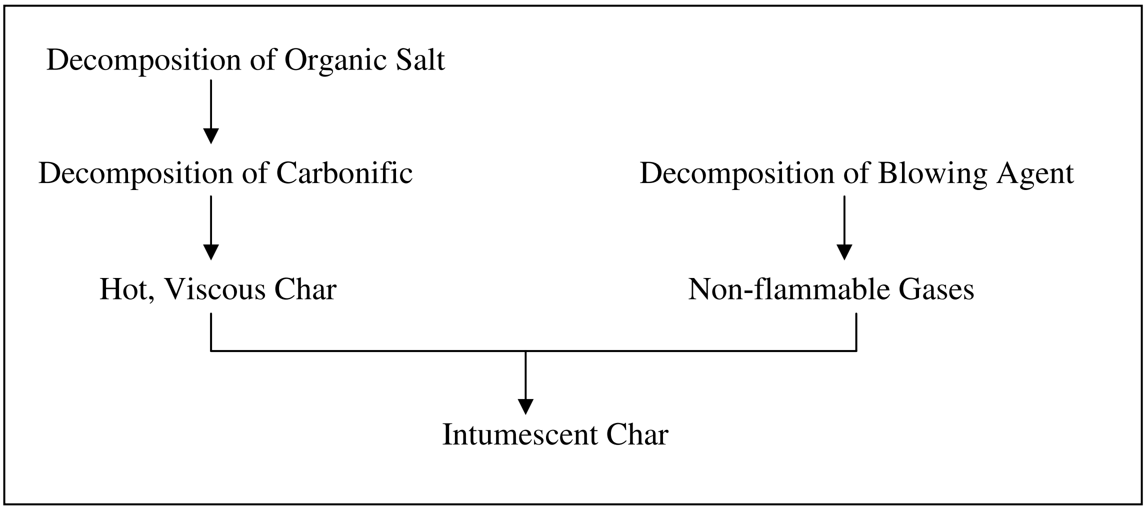


Figure 2.3 Sequence of intumescent reaction process (Vanderall, 1971)

The intumescence process commences with the decomposition of the inorganic salt or acid salt within the coating. The decomposition temperature of the acid must be sufficiently high that normal external heating (e.g. warming from direct sun-light) does not cause the coating to intumesce in the absence of fire, but the temperature must be below the pyrolysis temperature of the composite substrate. Furthermore, the acid must decompose before any other compound in the coating to ensure dehydration of the carbonific compound. The acid compounds used include zinc borate, linear high molecular-weight APP, melamine phosphate, organic esters, and salts of ammonium, amide or amine (Bourbigot et al., 1993; Castrovinci et al., 2005). These compounds decompose at between 100ºC and 250ºC, which is below the pyrolysis temperature of most organic resins used in composites. The decomposition reaction of the acid is catalysed by organic amides or amines.

The next stage is decomposition of the carbonific by a dehydration reaction with the decomposed inorganic salts. This reaction converts the carbonific into a carbonaceous char. The carbonific is a carbon-rich polyhydric compound that yields a large amount of char, and is usually a polycarbonate (such as starch or polyhydric alcohol) or phenol (such as phenol-formaldehyde). The hot and viscous char is then expanded with the decomposition of the blowing agent. Expansion of the char is dependent on decomposition of the carbonific and blowing agent occurring at the same temperature; otherwise the coating will fail to fully intumesce. The blowing agent decomposes via an endothermic reaction that produces a copious amount of non-flammable gases that cause the char melt to swell. Blowing agents are usually nitrogen compounds such as urea, dicyandiamide, guanidine, MEL and glycine that yield ammonia (NH_3), carbon dioxide (CO_2) and water (H_2O) vapour (Banerjee and Chattopadhyay, 1993). Chlorinated paraffin is also an effective agent that yields hydrogen chloride (HCl), CO_2 and H_2O vapour. The gases collect into small bubbles that cause the char to foam and swell. The coating eventually solidifies into a thick, multicellular material that slows the rate of heat conduction from the fire into the composite substrate.

A typical example of an intumescent coating is shown in Figure 2.4, and it has expanded to many times the original thickness. A good intumescent coating expands 50 to 200 times, and forms a fine-scale multicellular network with a cell size of 20 to 50 μm and wall thickness of 6-8 μm (Cullis and Hirschler 1981; Anderson et al., 1985). Quershi and Krassowski (1997) found that the addition of graphite flakes to an intumescent coating improved the fire resistance. The flakes expand up to 100 times on heating that produces a more effective insulating layer. The cell size can be controlled by the addition of inert fillers that assist the cell nucleation process. The addition of fillers such as titanium oxide and silica reduce the average diameter of the cells. The exact chemical compositions of the compounds used in commercial intumescent coatings are closely guarded by manufacturers, and while there is a wide choice of compounds from which to formulate intumescent compositions, only a few are used in practice (Vandersall, 1971). In addition to the compounds that control the intumescent process, the coating may contain other additives for purposes other than intumescence. For example, coatings may contain antioxidants, thickeners, coalescing agents, pigments for colouring, and milled fibres for structural reinforcement.

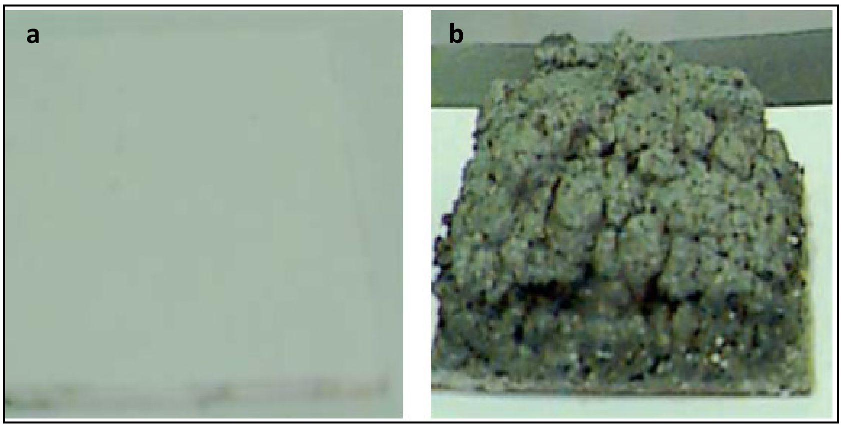


Figure 2.4 Intumescent coating (a) before fire test and (b) after fire testing (Anderson et al., 1985)

Intumescent coatings are excellent heat insulators that slow the rate of heat transfer into the substrate in a fire. Figure 2.5 compares the temperature rise in a composite panel with and without such a coating. The temperature was measured at the back-face of the panel. Intumescent coatings can be extremely effective in delaying combustion, suppressing flame spread, reducing heat release rate, and lowering the smoke density of composite materials (Zhang et al., 2009; Wang et al., 2010). While intumescent coatings are effective at protecting composite materials from heat and flame, they have several disadvantages. A major problem with many commercial coating products is that they do not bond strongly with the substrate, and often fall off during swelling, exposing the underlying composite directly to the flame. This is a common occurrence when a coating is applied to vertical (e.g. walls) or overhead (e.g. ceiling) structures. It is essential that the coating is bonded strongly to the substrate and has mechanical strength to ensure adequate fire protection. Further problems with intumescent coatings can include their incompatibility with certain manufacturing processes, poor aesthetic features, poor durability, rapid ageing by weathering (e.g. UV radiation, moisture absorption), and low resistance to wear and erosion.

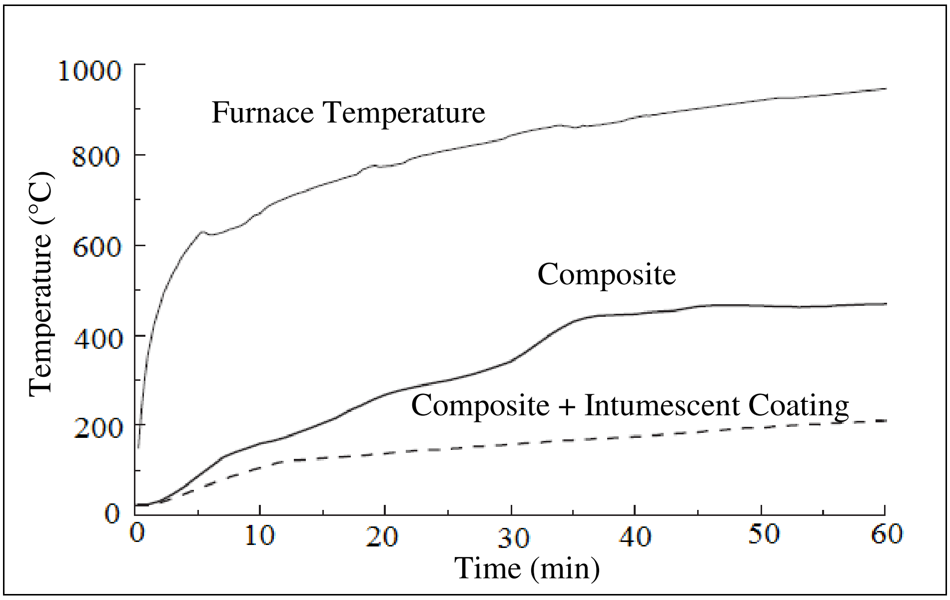


Figure 2.5 Composition of the back-face time-temperature profiles of a composite panel with and without an intumescent coating when exposed to fire

The optimization of intumescent formulations based on a thermoset epoxy-amine system as well as the characterization of its performance on steel has been conducted by Jimenez and his co-workers (2006a and 2006b). Two fire retarding agents were incorporated, separately or combined: a mineral acid (boric acid) and a commercial APP. It was observed that the use of the formulation without fire retardants provides properties close to those of the virgin steel plate only. When APP is added to the formulation, an improvement in fire protection performance is observed. However, the char does not adhere to the steel plate and falls off, resulting in failure to protect the steel. Similarly, boric acid yields enhanced the fire protection performance, but once more, the char falls off the plate. Finally, a combination of these two fire-retardant additives was incorporated into the system, resulting in the best properties while maintaining adherence of the char to the plate. It is revealed that in this thermoset epoxy-amine system, the combination between APP and boric acid led to the best protective results. The enhanced behaviour was attributed in particular to the combination of phosphates promoting adhesion to steel and of borates which produce a very hard char, resulting in the formation of borophosphates. The incorporation of boric acid in the formulation led to an increase in viscosity by creation of a hard glass (boron oxide), which traps gases and allows a char with good mechanical resistance.

2.5 Intumescent Flame Retardants

Intumescence is an interesting phenomenon. The French verb *tumere* means to ‘swell’. The Latin equivalent tumescere can be translated as ‘to swell up’. Therefore, tumid or tumescent means swollen or bulging, and the process of getting to a swollen state is intumescence (Mount, 1992). Intumescence is defined as the swelling of certain substances when they are heated. In flame retardant terms, exposure to fire or heat initiates a series of chemical and physical processes, leading to an expanded multicellular layer, which acts as a thermal barrier that effectively protects the structural elements against a rapid increase of temperature, thereby prevent the building from the collapse under severe fire conditions (Duquesne et al., 2004). This state is characterized by fire-resistant insulating foam. The foam serves to isolate heat and oxygen from the fuel source, extinguishing the fire.

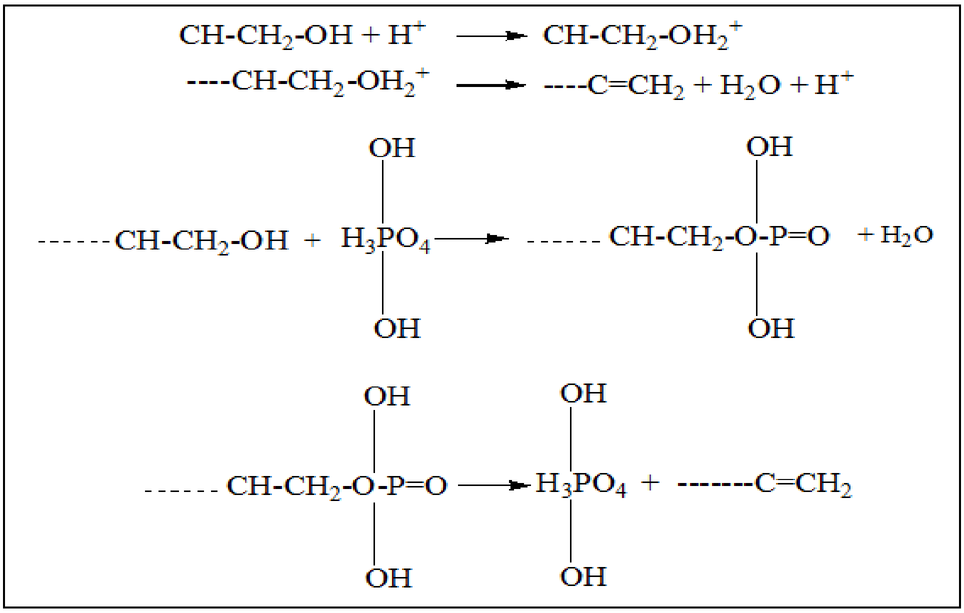
Flame retardant materials by intumescence are essentially a special case of a condensed phase mechanism. A complete description of intumescence requires analysis of both chemical and physical process. Different mechanisms, such as flame inhibition, heat loss due to melt flow and dripping, surface obstructions with char formation, acid-catalysed dehydration and char enhancement have been identified. The formation of a charred layer plays a significant role in the performance of intumescent fire retardants.

Recently, Wang and Yang (2010b) also studied the influences of flame-retardant EG modified by polyethylene glycol (PEG) on fire protection of water-borne intumescent fire resistive coating. In this study, the modified expandable graphite (MEG) was used as a modifier to improve the fire protection of intumescent fire resistive coating. The fourier transform infrared spectroscopy (FTIR) spectra, TGA analysis and SEM images well demonstrated that the surface of EG flakes was successfully modified by PEG. The TGA results showed that the addition of EG and MEG could improve the thermal stability of the coatings and enhanced the anti-oxidation of the char layers at a high temperature. The XRF results showed that anti-oxidation of the coatings was improved by adding EG or MEG. The SEM images demonstrated that the cell size of the char layer increased and the cell size distribution of the char layer became narrow after adding MEG into the coating.

Fire-resistant coatings are mainly based on 'classical' intumescent systems, research in this field is very wide and many parameters in the formulation can be modified. Therefore, different intumescent formulations can be developed to meet the specific fire protection requirements, which depend strongly on the substrate used.

2.5.1 Chemical Mechanism of Intumescence

A suggested mechanism for char formation is discussed by Mount (1992). The chemistry is often written in terms of simple acid-catalysed and dehydration reactions. This is shown in the four reactions as shown in Figure 2.6.



$$CH\text{-}CH_2\text{-}OH + H^+ \longrightarrow CH\text{-}CH_2\text{-}OH_2^+$$

$$\text{----}CH\text{-}CH_2\text{-}OH_2^+ \longrightarrow \text{----}C{=}CH_2 + H_2O + H^+$$

$$\text{------}CH\text{-}CH_2\text{-}OH + H_3PO_4 \longrightarrow \text{------}CH\text{-}CH_2\text{-}O\text{-}P(OH)_2{=}O + H_2O$$

$$\text{------}CH\text{-}CH_2\text{-}O\text{-}P(OH)_2{=}O \longrightarrow H_3PO_4 + \text{-------}C{=}CH_2$$

Figure 2.6 Chemical mechanism of intumescence

The first two reactions show the depolymerisation catalysed by an acid. The second two shows the dehydration of the sample when phosphoric acid is present. Both reactions essentially lead to the same result by producing -----$C{=}CH_2$ fragments at the chain ends. These fragments condense to form carbon-rich char residues. Briefly stated, the way the phosphorous compound work is that they phosphorylate carbonifics such as PER to make polyol phosphates. These polyol phosphates can then break down to form the char layer (Weil, 1992).

The protection mechanism of intumescent systems is based on the formation of a charred layer acting as a physical barrier which slows down heat and mass transfer between gas and condensed phases. Intumescent systems decompose and form upon heating large amounts of thermally stable carbonaceous residue. A large improvement of flammability properties can be achieved using intumescent systems in coatings. Thermal protection is the main purpose of intumescent materials; heat transfer is limited by the formation of the intumescent shield. Swelling is crucial to the fire protective capabilities and a fundamental understanding of the mechanisms that cause expansion is important. Temperature gradients and heat transfer play a crucial role in intumescent behaviour. In particular, the effect of the growing bubbles on the temperature field cannot be neglected. To make the intumescent flame-retardant efficient, a proper selection of components is essential, namely char formers, carbonising, dehydrating substances and modifiers allowing obtaining a maximum degree of carbonization and thus an efficiency of the protective char. Furthermore, it is very important to select proper binder resins. The required components for intumescent coating production are shown in Table 2.1.

Table 2.1: The basic and essential components of intumescent flame-retardant system (Rains, 1994)

Function of components	Compounds
Carbonising substance With a considerable number of carbon atoms, thermal decomposition of which results in the formation of carbonaceous material having a large number of hydroxyl groups, able to be esterification with acids.	Polyhydric alcohols (erythritol and its oligomers (pentaerythritol, pentaerythritol dimer and trimer , arabitol, sorbitol, inositol), saccharides (glucose, maltose, arabinose) and polysaccharides (starch dextrin, cellulose), polyhydric phenols (rezorcinol).
Dehydrating agent Substance releasing during its thermal decomposition an acid which esterifies hydroxyl groups.	Phosphoric acid, its ammonium, aminic salt and esters (ammonium phosphate and polyphosphate, melamine and urea phosphate tributyl phosphate), boric acid and its derivatives (borax, ammonium borate).
Foam forming substance Releases large quantities of nonflammable gases during its thermal decomposition, thus forming foamed structure of carbonaceous layer.	Nitrogen or halogen compounds such as melamine and its phosphoric salts, urea, dicyandiamide, guanidine and its derivatives, glycine, chlorinated paraffins.
Binder resin	Amino, epoxy, acrylic, polyacetic-vinyl and polyurethane resins.
Solvents, stabilisers, etc.	Specific, chemical compounds depending on the kind of resin.

On the other hand, mechanisms of action of boric acid and of coated APP (pure APP coated with tris-2-hydroxyethyl isocyanurate (THEIC)) in intumescent epoxy-based formulation were studied by Jimenez and his coworkers (2006b). The mechanisms of the intumescent samples were tested by using analytical techniques including TGA and solid-state nuclear magnetic resonance (NMR) in order to better understand the behaviours of those flame retardants. In previous research, they detected that some reactions took place during the intumescence phenomenon between boric acid and APP upon heating. The research focuses on the analysis of the degradation of those sole components and on the study of their interaction. It is first shown that the THEIC increases the thermal degradation rate of APP. This enables the degradation products of boric acid and coated APP to react together, resulting in the formation of borophosphate. It is suggested that the formation of this product provides the superior mechanical resistance of the char and promotes the adhesion of the char on the steel plate.

2.5.2 Physical Model of Intumescence

Intumescent flame retardants were initially used in paints and coatings. Typical formulations contained a phosphorous compound such as APP, a char forming polyol such as PER along with a blowing agent such as MEL. A binder is also necessary to keep the compounds in contact with each other.

With such intumescent coatings, the burning coating as a block consisting of several separate layers can be visualised. The top char layer is followed by the intumescent front where the foaming reactions take place. Below is an unburned coating layer that still contains the flame retardant. The bottom layer represents the substrate that is being protected by the intumescent coating. The char-foam provides a physical barrier to heat and mass transfer, and therefore interferes with the combustion process (Gilman and Kashiwagi, 1997).

For a mixture to be an efficient intumescent system, three ingredients are needed (Bertelli et al., 1989; Camino et al., 1989; Camino et al., 1990).

- An inorganic acid (dehydrating agent);
- A carbon rich polyhydric material as char former (carbonific); and
- A blowing agent (spumific).

The ratios in which the different compounds are present are also of utmost importance. The optimum ratio must be determined experimentally. One or more of these substances could be replaced with others of the same class or group. Further studies showed that more effective intumescent systems are obtained when two or more of the elements required for intumescence are incorporated in the same molecular complex (Camino et al., 1990).

The effectiveness of the intumescent flame retardants is due to the foamed char formed on the surface of the burning material (Camino et al., 1989). The char acts as a physical barrier against heat transfer to the surface of the combustible material. The layer of char furthermore hinders the diffusion of oxygen to the site of combustion. Char formation lowers the rate of the temperature increase of the surface beneath the char as shown in Figure 2.7.

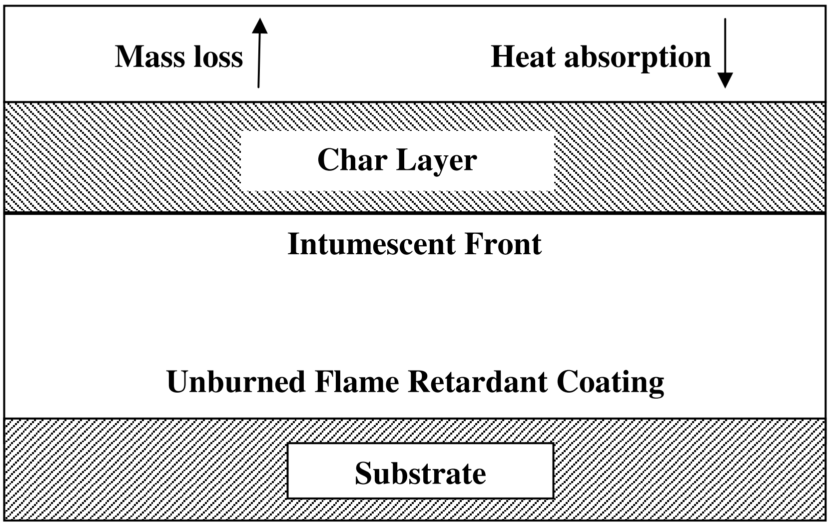


Figure 2.7 Schematic diagrams of the different layers during the burning process (Gilman and Kashiwagi, 1997)

Halogenated compounds such as chlorinated paraffin are commonly used in intumescent coatings as carbonifics. However, they are not widely used in intumescent flame retardants for plastics. Nitrogen based compounds are widely used owing to their environmental soundness. This is true for almost all char forming flame retardants have many advantageous over other systems because they produce less smoke and fewer toxic gases. The smoke is also less corrosive and the scrap more readily disposable after use (Horacek and Grabner, 1996). The shift to such environmentally friendly non-halogenated flame retardants are of a high interest worldwide. The market is trying to move away from halogenated flame retardants, but alternative systems are usually less effective or more expensive (Mount, 1992).

2.5.3 Phosphorus-Based Flame Retardants

The range of phosphorus-based flame retardant products is extremely wide, including phosphates, phosphonates, phosphinates, phosphine oxides, phosphates and red phosphorus. These phosphorated flame retardant agents can be used as additives or incorporated into the polymer chain during its synthesis, and are known to be active in the condensed and vapor phase.

In the condensed phase, the phosphorus-based flame retardants are particularly effective with polymers containing oxygen such as polyesters, polyamides and cellulose (Aronson, 1992; Weil, 2004). With most of them, thermal decomposition leads to the production of phosphoric acid, which condenses readily to produce pyrophosphate structures and liberate water as shown in Figure 2.8.

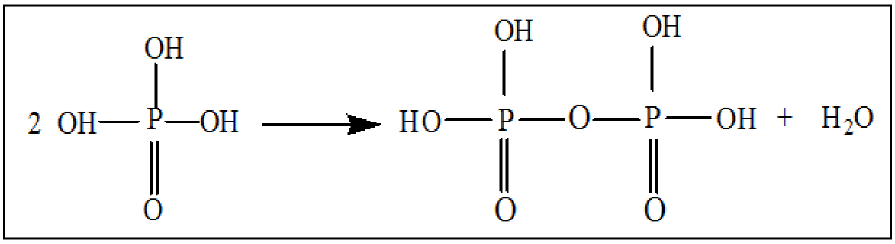


Figure 2.8 Pyrophosphate structure formations from phosphoric acid condensation

The water released dilutes the oxidizing gas phase. In addition, phosphoric acid and pyrophosphoric acid can catalyze the dehydration reaction of the terminal alcohols leading to the formation of carbocations and carbon-carbon double bonds as shown in Figure 2.9.

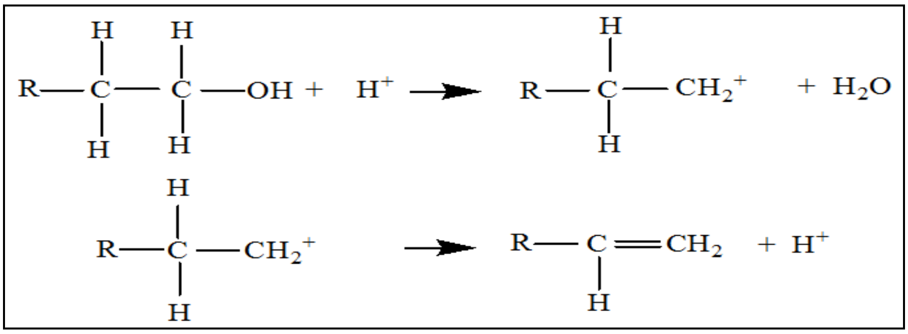


Figure 2.9 Formation of double carbon-carbon bonds after dehydration of alcohol and groups

At high temperature, ortho- and pyrophosphoric acids are turned into metaphosphoric acid ‘‘(O)P(O)(OH)’’ and their corresponding polymers ‘‘$(PO_3H)_n$’’. The phosphate anions (pyro- and polyphosphates) then take part, with the carbonized residues, in char formation. This carbonized layer (char) isolates and protects the polymer from the flames and:

- limits the volatilization of fuel and prevents the formation of new free-radicals;
- limits oxygen diffusion, which reduces combustion;
- insulates the polymer underneath from the heat.

Phosphorus-based flame retardants can also volatilize into the gas phase, to form active radicals (PO_2•, PO• and HPO•), and act as scavengers of H• and OH• radicals. Volatile phosphorated compounds are among the most effective combustion inhibitors since phosphorus-based radicals are, on average, five times more effective than bromine and 10 times more effective than chlorine radicals (Babushok and Tsang, 2000).

Phosphorus-based flame retardants are significantly more effective in oxygen or nitrogen containing polymers. It is thus important to have oxygen or nitrogen atoms in the polymer chain. If the polymer cannot contribute to charring because of the absence of suitable reactive groups, a highly charring co-additive has to be introduced in combination with the phosphorated flame retardant. This co-additive may be a polyol such as pentaerythritol (Camino, 1984). Some polymers such as polyamides or polyurethanes can also be used as charring agents in intumescent flame retardant systems.

Ammonium polyphosphate (APP) is an inorganic salt of polyphosphoric acid and NH_3. The chain length (n) of this branched or unbranched polymeric compound is variable; n can be higher than 1000. Short, linear chain APPs (crystalline form I: APP I) ($n < 100$) is more water sensitive (hydrolysis) and less thermally stable than a longer chain APPs (crystalline form II: APP II) ($n > 1000$), which exhibit very low water solubility (<0.1 g/ 100 ml) as shown in Figure 2.10.

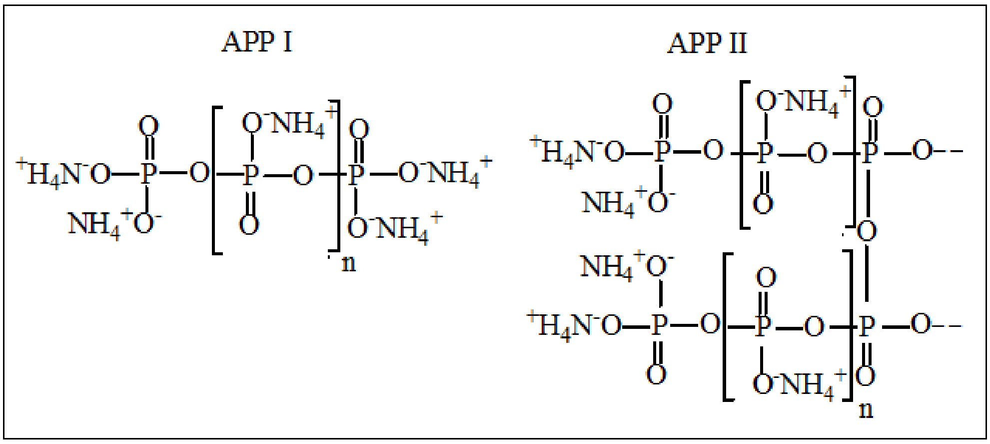


Figure 2.10 Chemical structure of APP I and APP II (Camino et al., 1978)

APPs are known to be stable and non-volatile compounds. Long chain APPs start to decompose into polyphosphoric acid and NH_3 at temperatures above 300ºC. Short-chain APPs begin to decompose at temperatures above 150ºC. It is therefore very important to adapt the crystalline form of the APP to the polymer decomposition temperature.

It is well known that the incorporation of APP in oxygen or nitrogen-containing polymers (polyesters (Shih et al., 2004), polyamides (Levchik et al., 1996) and polyurethane (Duquesne et al., 2001) leads to polymer charring. The thermal degradation of APP creates free acidic hydroxyl groups, which is condensed by thermal dehydration yielding a crosslinked ultraphosphate and a polyphosphoric acid with a highly crosslinked structure (Camino et al., 1978). The polyphosphoric acid reacts with the oxygen or nitrogen containing polymers and catalyzes their dehydration reaction and char formation. The effectiveness of APP depends also on the level of incorporation. At relatively low concentrations, APP is not efficient in aliphatic polyamides. However, it becomes very efficient at high concentration, e.g. >10% in polyamide-6, 6, >20% in polyamide-11, -12, -6, -10 and >30% in polyamide-6 (Levchik et al., 1996).

2.6 Flame Retardant Fillers

Particulate fillers can strongly influence the combustion characteristics of intumescent coatings, including its resistance to ignition, and the extent and nature of smoke and toxic gas emission products. This may result from simple dilution of the combustible fuel source, slowing down the diffusion rate of oxygen and flammable pyrolysis products and changing the melt rheology of the polymer, thereby affecting its tendency to drip. However, depending on the nature of the filler, the heat capacity, thermal conductivity and emissivity of the flame retardants composition may also change, giving rise to heat transfer and thermal reflectivity effects, which can also slow the rate of burning (Hornsby, 2007).

In general, fillers cannot be classed as totally inert in relation to their effect on flame retardant combustion. However, some notably metal hydroxides, hydrates and carbonates can confer additional flame retardancy and smoke suppressing qualities being in widespread use for this purpose. These undergo endothermic decomposition, which cools the solid or condensed phase, and release gases, which dilute and cool flammable combustion products in the vapour phase. The inorganic residue remaining after filler decomposition may also be highly significant in providing a thermally insulating barrier between the underlying polymer substrate and external heat source, in addition to contributing to overall smoke suppression. In this connection, material, which are currently used or have been potential for use as fire-retardant fillers, are listed in Table 2.2, together with relevant thermal properties and gaseous products evolved on decomposition.

Table 2.2: Current and potential fire retardant filler (Rothon, 2003)

Candidate material (common names and formula)	Approximate onset of decomposition (°C)	Approximate enthalpy of decomposition (kJg^{-1} x 10^3)	Volatile content (%w/w)		
			Total	H_2O	CO_2
Nesquehonite [$MgCO_3 \cdot 3H_2O$]	70-100	1,750	71	39	32
Alumina trihydrate, aluminium hydroxide [$Al(OH)_3$]	180-200	1,300	34.5	34.5	0
Basic magnesium carbonate, Hydromagnesite [$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$]	220-240	1,300	57	19	38
Sodium dawsonite [$NaAl(OH)_2CO_3$]	240-260	Not available	43	12.5	30.5
Magnesium hydroxide [$Mg(OH)_2$]	300-320	1,450	31	31	0
Magnesium carbonate subhydrate [$MgO \cdot CO_{2(0.96)}H_2O_{(0.30)}$]	340-350	Not available	56	9	47
Calcium hydroxide[$Ca(OH)_2$]	430-450	1,150	24	24	0
Boehemite [$AlO(OH)$]	340–350	560	15	15	0
Magnesium phosphate Octahydrate [$Mg_3(PO4)_2 \cdot 8H_2O$]	140–150	Not available	35.5	35.5	0
Calcium sulphate dihydrate, gypsum [$CaSO_4 \cdot 2H_2O$]	60-130	Not available	21	21	0

In addition to their fire-retarding efficiency, to be commercially exploitable, these fillers should ideally be inexpensive, colourless, non-toxic, free from conductive contaminants, and readily available. However, to achieve the maximum fire-retarding effect, thermal decomposition should generally occur near the onset of flame retardant degradation, with a subsequent release of flammable volatiles.

The size and shape of the filler particles are also important considerations. Filler particle size and the need to use high addition levels to confer adequate fire retardancy create particular limitations on their potential use in intumescent fire protective coating, both in terms of their processability and ultimate physical properties.

Any type of inorganic filler, even inert, can influence the reaction of intumescent coatings to fire for several reasons (Hornsby, 2007):

- it reduces the content of combustible products,
- it modifies the thermophysical properties and thermal conductibility of the resulting material;
- it changes the viscosity of the resulting material;
- it removes a good deal of the heat evolved in a degradation and thus can prevent further degradation. To be effective, they must be used at very high loadings, which lead in some instances to the loss of mechanical properties of interest.

All these actions have an indirect incidence on the intumescent coatings fire performance. Nevertheless, some minerals are more specifically used as flame retardants owing to their behavior at high temperature. The most commonly used mineral flame retardants are metal hydroxides (especially of aluminum and magnesium), hydroxycarbonates and zinc borates. Besides the aforementioned general effects, these inorganic fillers have a direct physical flame retardant action. As the temperature rises, these fillers decompose endothermically and therefore absorb energy. Moreover, they release non-flammable molecules (H_2O and/or CO_2), which dilute combustible gases, and can also promote the formation of a protective ceramic or vitreous layer.

2.6.1 Chicken Eggshell (CES) as Bio-filler

CES contains about 95% calcium carbonate ($CaCO_3$) in the form of calcite and 5% organic materials such as sulfated polysaccharides, type X collagen, and other proteins (Arias and Fernández, 2003). The effect of filler ($CaCO_3$) on the fire retardancy of intumescent polypropylene compounds has been studied. Addition of $CaCO_3$ as a filler increases the residual weight and forms a protective char layer during chemical reaction. The results show that calcium carbonate has ability to improve the fire protective performance. Although there have been several attempts to use eggshell components for different applications, its chemical composition and availability makes eggshell a potential source of filler for polypropylene composites.

2.7 Binder in Intumescent Coatings

The influence of the binder in water-borne coatings was recently studied by Wang and Yang (2010b). An epoxy emulsion was combined with a self-crosslinked silicone acrylate (SSA) emulsion to get a water-borne intumescent coating. In this system, the well-known APP/PER/MEL intumescent system is combined with titanium dioxide (TiO_2), kaolin and expandable graphite (EG). The samples were tested by recording the temperature on the back of a heated plate. The shape of temperature profiles is similar in all the coatings. At the beginning of the test, there is almost no difference between them, then, after 20 minutes, a steady state is reached, and its temperature depends on the coating formulation: for epoxy/SSA ratios ranging from 39/0 to 33.4/5.6, the temperature is gradually decreased from 270°C to 243°C. Subsequently, the SSA content increases further. The tendency reverses and the temperature reaches 290°C. Because the efficiency of an intumescent coating is also linked to the morphology of the char, SEM showed that reasonable amount of SSA in the system led to the formation of dense foam. Too big amount of SSA gives rise to large cells, therefore decreasing the insulation, as was observed during the fire test.

The binder in the intumescent coating is important due to its two effects: it contributes to the formation of a uniform foam structure and char layer expansion (Wang and Yang, 2010b). The type of binders currently used in intumescent coating such as polyvinyl acetate emulsion, vinyl chloride latex, alkyd resin and acrylic resin. These binders even have good performance but their chemical compositions produce high amount of toxic gases and smoke when expose to fire. In this study, the water based epoxy emulsion and silica fume as mixed binder were used in order to minimize the smoke and toxic fume emission without compromising on quality and effectiveness of intumescent coating in fire protection.

2.7.1 Silica Fume as Binder

Silica fume which is a by-product in the manufacturing process of ferro silicon and metallic silicon was used as siliceous admixture and water reducing agent was employed as chemical admixture. The chemical analysis and physical properties of silica fume are listed in Table 2.3.

Table 2.3: Physical properties and chemical composition of silica fume

Physical Properties								
Density (g/cm^3)		Particle size (µm)		Specific Surface (m^2/g)				
2.2		0.1 to 0.2		18 to 20				
Chemical Composition (%)								
1g. Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	S	C	K_2O	Total
0.36	95.5	0.35	0.61	0.4	0.1	2	0.5	100

In recent times, the silica fume is widely used as an additional binder material in cement mortar and concrete all over the world in the production of high strength and durable mortar (Sabir, 1997; Duval and Kadri, 1998; Taheri and Breugel, 1998; Nakamoto et al., 1998). In this research, silica fume was proposed as an additional binder on developing water-borne intumescent fire protective coating due to its high thermal stability, good dispersion in water as well as economical binder material.

2.8 Temperature Effects on Steel

Steel is a metal alloy whose major component is iron, with carbon being the primary alloying material. Different quality/grades of steel can be manufactured by varying the amount of carbon and its distribution in the alloy (Sakumoto, 1999). Fire resistant steel is manufactured by adding molybdenum (Mo) and other alloying materials. The behavior of steel when exposed to high temperatures is of critical importance for the safety and stability of the building. The temperature rise for a steel member is a function of the materials, thermal conductivity and specific heat (Wong and Ghojel, 2003).

When steel is exposed to fire, the steel temperature increases resulting in the reduction of the strength and stiffness of the steel. This material response to fire can lead to possible deformations and failure, depending on the applied loads, temperature profile, and support conditions. The increase in steel temperature depends on the severity of the fire, the section factor (area of exposed steel) and the amount and type of applied fire protection materials.

In general, unprotected steel structures perform poorly in fires relative to other structural materials such as concrete, gypsum, and timber. This poor performance can be partly attributed to the thinner elements used, the higher thermal conductivity of steel and high thermal expansion (Buchanan, 2001).

In this section, elevated temperature provisions from Eurocode will be discussed. Unlike most codes which follow a prescriptive method for accounting for fire loading, Eurocode 3: Part 1-2 (EC3, 2005) presents a design recommendation for structural members exposed to fire. Eurocode 3 puts forth performance requirements that are as follows:

i. Where mechanical resistance in the case of fire is required, steel structures shall be designed and constructed in such a way that they maintain their load bearing function during the relevant fire exposure.

ii. Deformation criteria shall be applied where the means of protection, or the design criteria for separating members, require consideration of the deformation of the load bearing structure.

These performance criteria are carried out through the use of reduction factors for the material at elevated temperature, which are presented in Section 3 in Eurocode 3: Part 1-2. This concept is used in Eurocode to develop reduction factors for various elevated temperatures. There is a detailed structural fire design procedure, which is presented in Section 4 in Eurocode 3: Part 1-2. In this section, both a simple calculation model and an advanced calculation model are discussed.

Table 2.4 gives reduction factors relative to the appropriate value at ambient temperature, as developed in Eurocode 3, for the stress-strain relationship shown in Figure 2.12. In this case, ambient temperature is 20°C (68°F). The reduction factors given in Table 2.4 are defined as follows:

-effective yield strength, relative to yield strength at 20°C: $k_{y,\theta} = f_{y,\theta}/f_y$ (2.1)

-proportional limit, relative to yield strength at 20°C: $k_{p,\theta} = f_{p,\theta}/f_y$ (2.2)

-slope of linear elastic range, relative to slope at 20°C: $k_{E,\theta} = E_{a,\theta}/E_a$ (2.3)

Table 2.4: Reduction factors for stress-strain relationship of carbon steel at elevated temperatures (EC3, 2005).

Steel Temperature θ_a	Reduction factors at temperature θ_a relative to the value of f_y or E_a at 20°C		
	Reduction factor (relative to f_y) for effective yield strength $k_{y,\theta} = f_{y,\theta} / f_y$	Reduction factor (relative to f_y) for proportional limit $k_{p,\theta} = f_{p,\theta} / f_y$	Reduction factor (relative to E_a) for the slope of the linear elastic range $k_{E,\theta} = E_{a,\theta} / E_a$
20°C	1,000	1,000	1,000
100°C	1,000	1,000	1,000
200°C	1,000	0,807	0,900
300°C	1,000	0,613	0,800
400°C	1,000	0,420	0,700
500°C	0,780	0,360	0,600
600°C	0,470	0,180	0,310
700°C	0,230	0,075	0,130
800°C	0,110	0,050	0,090
900°C	0,060	0,0375	0,0675
1000°C	0,040	0,0250	0,0450
1100°C	0,020	0,0125	0,0225
1200°C	0,000	0,0000	0,0000

The properties on the stress-strain diagram shown in Figure 2.11 are defined as below.

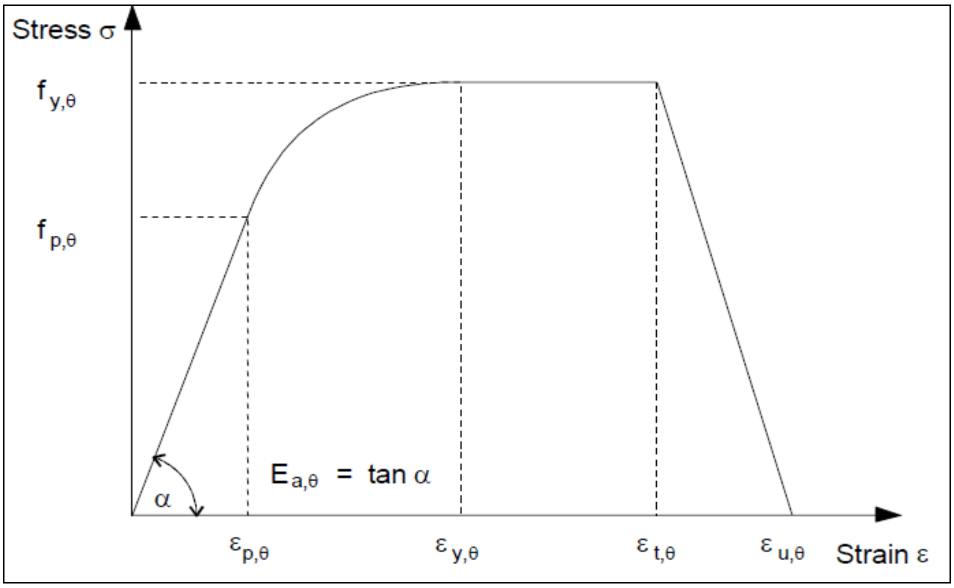


Figure 2.11 Stress-strain relationships for carbon steel at elevated temperatures (EC3, 2005)

Key: $f_{y,\theta}$ = effective yield strength

$f_{p,\theta}$ = proportional limit

$E_{a,\theta}$ = slope of the linear elastic range

$\varepsilon_{p,\theta}$ = strain at the proportional limit

$\varepsilon_{y,\theta}$ = yield strain

$\varepsilon_{t,\theta}$ = limiting strain for yield strength

$\varepsilon_{u,\theta}$ = ultimate strain

The variation of the reduction factors with temperature for the stress-strain relationship of steel at elevated temperatures from Table 2.4 is plotted in Figure 2.12. Note that at a temperature a little above 400°C (approximately 800°F); there is a significant reduction in the yield strength, slope of linear elastic range, and proportional limit. It is of particular interest in this research to determine if the metal behaves like the base metal at elevated temperature, particularly experiencing a significant reduction in strength at approximately 800°F. Alternatively, for temperatures below 400°C, the stress-strain relationship specified may be extended by the strain-hardening, provided local or member buckling does not lead to premature collapse (EC3, 2005).

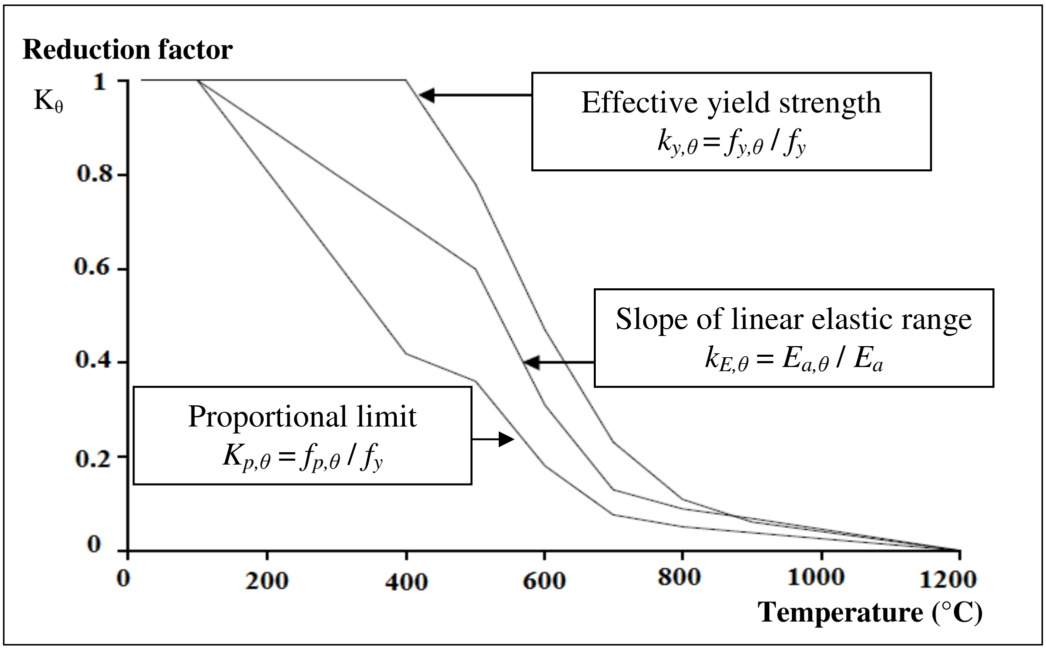


Figure 2.12 Reduction factors for the stress-strain relationship of carbon steel at elevated temperature (EC3, 2005)

2.9 Standard Time-temperature Fire Tests on Steel

Most countries around the world rely on fire resistance tests to determine the performance of building materials and structural elements during a fire. The time-temperature curve used in fire-resistance tests is called the 'standard fire'. The most widely used fire curves that have been recognized as a standard for fire testing is ASTM E-119 (ASTM 1988), ISO 834 (ISO, 1975) and Eurocode. Most national standards are based on either the ASTM E-119 test or the ISO 834 test. In this research, the Eurocode parametric time-temperature curve (EC1, 2002) was chosen as a standard time-temperature curve for furnace test due to its limitation requirements to meet the ASTM E-119 and the ISO 834 standard time-temperature curves. In this study, the fire standards are described briefly, and it is not the purpose of this chapter to give an exhaustive description of all the standard fire curves.

2.9.1 The Eurocode Time-temperature Curve

Parametric fire curves are described in Eurocode 1 part 1-2 (EC1, 2002). They provide a more rational indication of compartment temperatures than those prescribed by nominal fire curves. The Eurocode gives an equation for 'parametric' fires, allowing a time-temperature relationship to be produced for any combination of fuel load, ventilation openings and wall lining materials. The equation for the heating phase of the Eurocode parametric time-temperature curve is as follows.

$$T_m = 1325(1 - 0.324\exp^{-0.2t} - 0.204\exp^{-1.7t} - 0.472\exp^{-19t}) + T_a°C. \qquad (2.4)$$

where T_m, maximum temperature and T_a, ambient temperature (°C).

The Eurocode parametric time-temperature curve as shown in Figure 2.13 is the most common time-temperature curve that is used for fire testing.

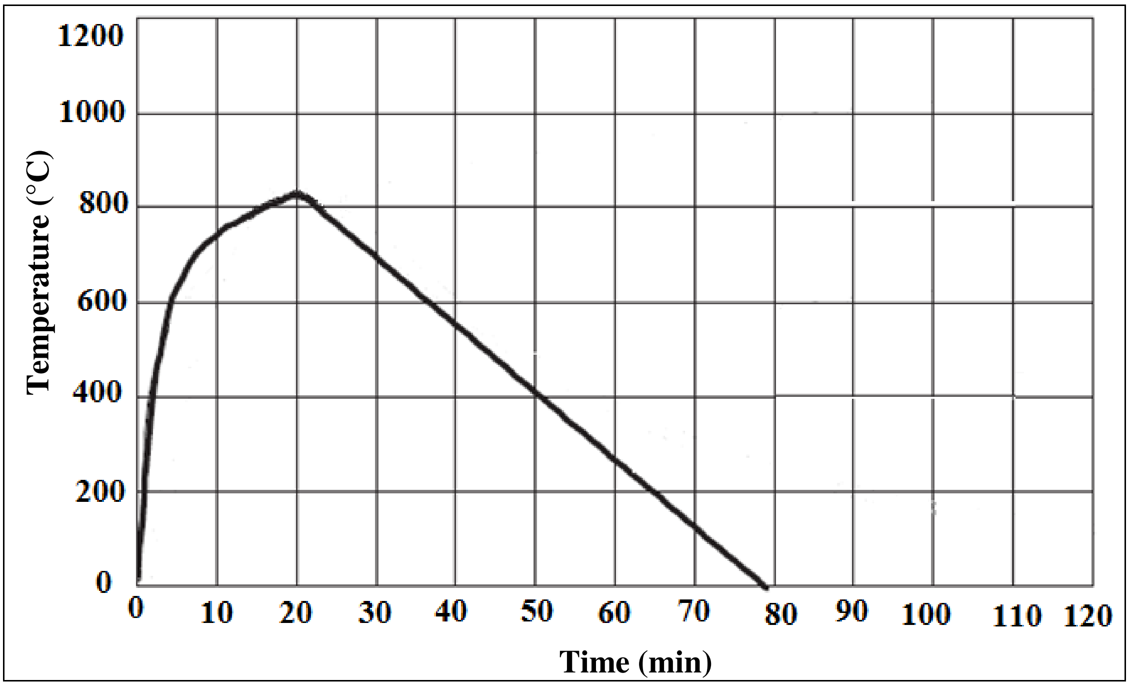


Figure 2.13 Eurocode parametric time-temperature curve (EC1, 2002)

2.9.2 ASTME-119 Time-temperature Curve

ASTM E-119 (ASTM 1988) is a widely recognized standard for fire testing in the United States. The first edition was published in 1918, with the most recent published in 2000 (Lane, 2000). Technical committees help in setting up a standard, and this standard is revised as technology and understanding changes. There has been significant debate on the validity of ASTM E-119 data and methodology due to the recent events of 9/11. One has to understand that ASTM E-119 is a guideline for fire-safe design of buildings and not a predictor of behavior in an actual fire. Real fires are a function of many variables, such as fuel load, thermal radiation, heat flux, ventilation factor, and area of openings, which are related to the type of construction, building occupancy, and design (Lie, 1978; Lane, 2000; Wong and Ghojel, 2003). The time-temperature profile for ASTM E-119 is shown in Figure 2.14. The main purpose of using the ASTM E-119 protocol is to establish and document the fire rating of different elements of a building. The test does not cover flame spread, fuel contribution, or smoke density.

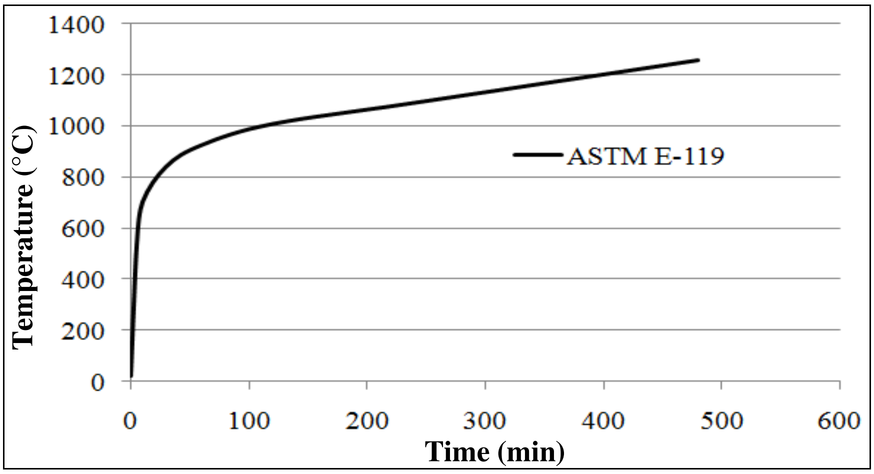


Figure 2.14 ASTM-119 time-temperature curve (ASTM, 1988)

The American ASTM E-119 fire curve is not described as an equation, but rather by a series of data points as shown in Table 2.5, which give temperature values at different times (Buchanan, 2002).

Table 2.5: Time-temperature curve as specified by the ASTM E-119 (1988), reported by Buchanan (2002)

Time (min)	ASTM E-119 Temperature (ºC)
0	20
5	538
10	704
30	843
60	927
120	1010
240	1093
480	1260

2.9.3 ISO 834 Standard Time-temperature Curve

The corresponding standard curve prescribed by the International Standards Organization, ISO 834 is produced by the equation following equation and is displayed in Figure 2.15.

$$\theta_g = 20 + 345\log\left(8t + 1\right) \quad (2.5)$$

where, θ_g = furnace temperature $\left({}^{o}\mathrm{C}\right)$
t = time (*minutes*)

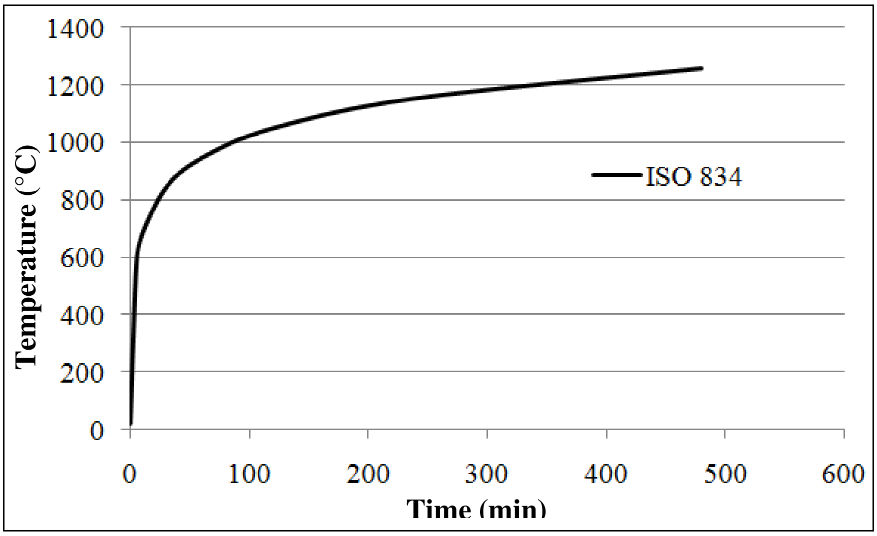


Figure 2.15 ISO 834 time-temperature curve (ISO, 1975)

The furnace and time-temperature exposure is nearly identical but ISO 834 does not include a hose stream test. There is also a difference in the furnace pressures. ASTM El19 is operated at a negative pressure and IS0 834 at a positive pressure.

Table 2.6: Time-temperature curves as specified by the ISO 834 standards (1975), reported by Buchanan (2002)

Time (min)	ISO 834 Temperature (ºC)
0	20
5	576
10	678
30	842
60	945
120	1049
240	1153
480	1257